Diels-Alder Addition of N,N-Diethyl-1,3-butadienylamine to Dehydroaromatic Intermediates Generated from Some Haloaromatics (Commemoration Issue Dedicated to Professor Tatsuo Yamamoto on the Occasion of his Retirement)

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Diels-Alder Addition of N,N-Diethyl-1,3-butadienylamine to Dehydroaromatic Intermediates Generated from Some Haloaromatics

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Diels-Alder addition of N,N-diethyl-1,3-butadienylamine (DBA) to dehydroaromatic intermediates, generated from some aromatic halo ethers and sulfides, was investigated. The primary Diels-Alder adducts lose diethylamine and aromatize. The same reaction using 4-chlorobiphenyl (**1h**), N,N-dimethyl-*p*-bromoaniline(**1i**) or 9-bromophenanthrene(**1j**) was also investigated.

KEY WORDS: Diels-Alder reaction/ Reaction of N,N-diethyl-1,3-butadienylamine/ Reaction of dehydrobenzene/

We have previously described[1] the Diels-Alder addition of amino derivatives of 1,3-butadiene to arynes generated *in situ* from haloaromatics such as halobenzene, halotoluene or halonaphthalene with $NaNH_2$. This is a convenient one-step procedure for the preparation of naphthalene, methylnaphthalene or phenanthrene from halobenzene, halotoluene or halonaphthalene, respectively.

It is an interesting subject to investigate whether this procedure can be extended to include the other haloaromatics which furnish dehydroaromatic intermediates with strong base. Furthermore, recent communications on closely related topics[2,3] have prompted us to report our results on the reaction of N,N-diethyl-1,3-butadienylamine(DBA)[4] to the arynes, generated *in situ* from some aromatic halo ethers with $NaNH_2$ or KO-*t*-Bu. Besides these readily available aromatic halo ethers(**1a-e**), methyl *p*-chlorophenyl sulfide(**1f**), ethyl *p*-chlorophenyl sulfide(**1g**), 4-chlorobiphenyl(**1h**), N,N-dimethyl-*p*-bromoaniline(**1i**) and 9-bromophenanthrene (**1j**) were also used as starting haloaromatics. The procedure using *o*-chloroanisole, *p*-dichlorobenzene or *p*-chloroacetanilide was unsuccessful, probably because none of these haloaromatics furnish the corresponding dehydroaromatic intermediate under given basic conditions.

The primary Diels-Alder adducts are easily transformed. Thus the adducts lose diethylamine and aromatize. By comparing the structures of end products with those of starting haloaromatics, it is apparent that this procedure is somewhat specific in its ability to convert a halobenzene moiety of haloaromatics into a naphthalene moiety. In other words, the Diels-Alder additions with DBA and arynes have found useful synthetic application as a means of adding anellated benzene

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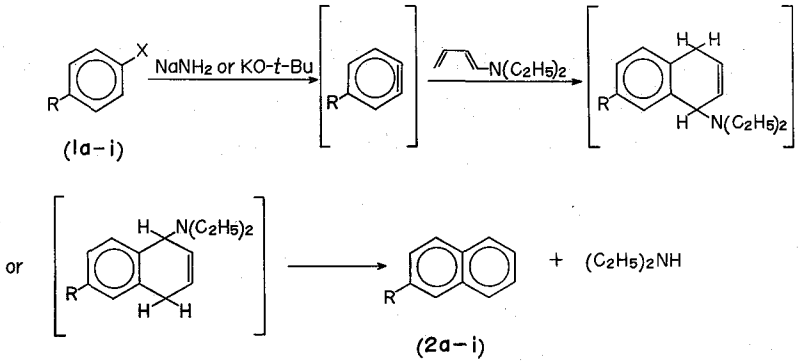
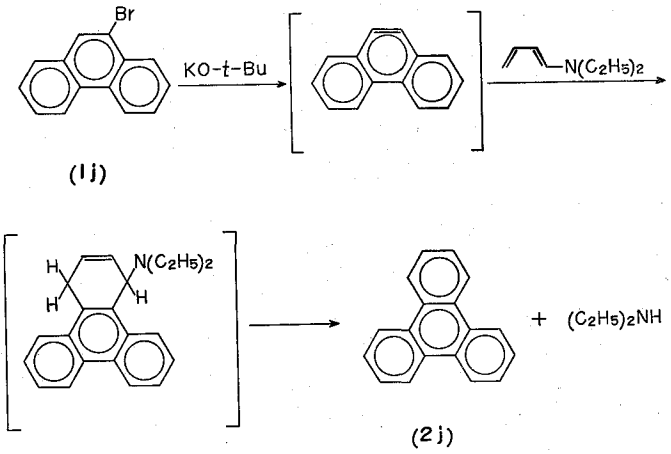


(**a**) R=OCH_3; X=Cl, (**b**) R=OC_2H_5; X=Cl, (**c**) R=$O(CH_2)_2CH_3$; X=Cl, (**d**) R=OCH_3; X=Br, (**e**) R=OC_6H_5; X=Br, (**f**) R=SCH_3; X=Cl, (**g**) R=SC_2H_5; X=Cl, (**h**) R=C_6H_5; X=Cl, (**i**) R=$N(CH_3)_2$; X=Br



ring. The concurrently produced diethlyamine in these reactions further add to dehydroaromatic intermediates prior to the escape from the reaction mixtures. It is easy to understand the occurrence of the side reaction through the paper we have already published[1] and the others.[5,6]

As indicated in Table I, DBA, which is also a reaction partner, was advantageously used as solvent for the reactions with $NaNH_2$, and for those with KO-*t*-Bu was used a proper amount of distilled toluene.

In the reaction between bromobenzene and DBA, the best yield was achieved[1] by using 3 equivalents $NaNH_2$ to the bromobenzene, wherein all of the charged bromobenzene was consumed. However, a relatively high percentage of starting haloaromatics has been recovered unchanged in the most part of the reactions listed in Table I even when the applied $NaNH_2$ (or KO-*t*-Bu) is 6 equivalents (especially, in Runs 2, 4, 6, 7 and 8). For the reaction of bromobenzene with DBA, $NaNH_2$ is more suited than KO-*t*-Bu as base. The same holds the reaction of *p*-chloroanisole (**1a**) with DBA (Run 1 versus Run 2). However, none of the objective pro-

Table I. Diels-Alder Addition of N,N-Diethyl-1,3-butadienylamine (DBA) to Dehydroaromatic Intermediates

Run[a]	Abbreviation of starting haloaromatics	Base (Mole ratio of haloaromatics: base)	Solvent	Reaction temperature (Time)	Product[b] Abbreviation	Product[b] Yield[c] (%)
1	**1a**	$NaNH_2$(1:6)	DBA	100–110°C (7 hr)	**2a**	40
2	**1a**	KO-*t*-Bu(1:6)	Toluene	Reflux (8 hr)	**2a**	10[d]
3	**1b**	$NaNH_2$(1:6)	DBA	100–110°C (7 hr)	**2b**	22[d]
4	**1c**	KO-*t*-Bu(1:6)	Toluene	Reflux (8 hr)	**2c**	12[d]
5	**1d**	$NaNH_2$(1:6)	DBA	100–110°C (7 hr)	**2d**[e]	30[f]
6[g]	**1e**	$NaNH_2$(1:6)plus KO-*t*-Bu(1:3)	Toleune	Reflux (8 hr)	**2e**	20[d]
7	**1f**	KO-*t*-Bu(1:6)	Toluene	Reflux (9 hr)	**2f**	9[h]
8	**1g**	KO-*t*-Bu(1:6)	Toluene	Reflux (9 hr)	**2g**	8[h]
9	**1h**	$NaNH_2$(1:6)	DBA	100–110°C (7 hr)	**2h**	21[d]
10[i]	**1i**	$NaNH_2$(1:6)	DBA	100–110°C (7 hr)	**2i**	21[j]
11	**1j**	KO-*t*-Bu(1:6)	Toluene	Reflux (7 hr)	**2j**	35[h]

a) All runs were conducted under a nitrogen atmosphere. b) All spectral data (nmr, ir and mass spectral) of the isolated products were consistent with assigned structures, and if possible, these data were compared with those of authentic compounds. c) Yield was based upon starting haloaromatics, and was of the isolated pure product. d) Isolated by column chromatography on silica gel in 10%dichloromethane-90%hexane. e) **2d** is identical to **2a**. f) Isolated by column chromatography on silica gel in 10%ether-90%hexane. g) In the reaction with $NaNH_2$ alone as base, the yield of phenyl *β*-naphthyl ether (**2e**) was only 9%. h) Isolated by column chromatography on silica gel in hexane. i) Only when **1i** was used as haloaromatics, the post-treatment of the reaction mixture was as follows. At the conclusion of the reaction, the mixture was poured into a mixture of ice water and ether. The aqueous layer was removed, and the organic layer was extracted with three portions of 100 ml of 7%HCl. The combined 7%HCl extracts were made basic with aqueous Na_2CO_3 and again extracted with ether. The ether extract was dried over $MgSO_4$ and the ether was evaporated. The objective, N,N-dimethyl-*β*-naphthylamine (**2i**) could be separated by column chromatography on silica gel. j) Isolated by column chromatography on silica gel in 35% dichloromethane-65%hexane.

duct was obtained by using $NaNH_2$ as base for the reaction of *n*-propyl *p*-chlorophenyl ether (**1c**), **1f**, **1g**, or **1j** with DBA.

EXPERIMENTAL

Illustrative examples of the reactions are given below.

Addition of N,N-Diethyl-1,3-butadienylamine(DBA) to 3,4-Dehydroanisole Generated from *p*-Chloroanisole(1a) with $NaNH_2$. To a stirred mixture containing 15 g(0.12 mol) of DBA and 2.9 g(0.02 mol) of **1a** was added 4.7 g (0.12 mol) of $NaNH_2$, and then stirred for 7 hr at 100–110°C in a nitrogen atmosphere.

The dark-brown reaction mixture was cooled and slowly poured into a mixture of ice water and ether. The aqueous layer was removed, and the ether extract was washed with three portions of 100 ml of 7 %HCl, and once with 100 ml of water. After drying over $MgSO_4$, the ether extract was evaporated to yield 1.3 g (40 %) of methyl β-naphthyl ether(**2a**), mp 66–68°C (from hexane).

Addition of N,N-Diethyl-1,3-butadienylamine(DBA) to 9,10-Dehydrophenanthrene Generated from 9-Bromophenanthrene(1j) with KO-*t*-Bu. To a solution containing 15 g(0.12 mol) of DBA and 5.1 g(0.02 mol) of **1j** in 70–80 ml of toluene is added 13.5 g(0.12 mol) of KO-*t*-Bu, and the mixture was refluxed for 7 hr in a nitrogen atmosphere. The brown colored reaction mixture was cooled and poured into a mixture of ice water and ether. The aqueous layer was removed, and the ether extract was washed successively with three portions of 100 ml of 7 % HCl, 100 ml of water, and 100 ml of dilute aqueous $NaHCO_3$. After drying over $MgSO_4$ and evaporating the solvents, the obtained crude triphenylene (**2j**) was purified by column chromatography on silica gel in hexane. Yield 1.6 g (35 %), mp 194–195.5°C.

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